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Synthesis, isomerism, and catalytic properties of chelate ruthenium copper bimetallacarborane cluster *exo-closo*-$(Ph_3P)Cu(\mu\text{-}H)Ru[Ph_2P(CH_2)_4PPh_2](\eta^5\text{-}C_2B_9H_{11})$, in radical polymerization of methyl methacrylate*

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Chelate *exo-nido*-ruthenacarboranes *exo*-5,6,10-$[RuCl(Ph_2P(CH_2)_4PPh_2)]$—5,6,10-$(\mu\text{-}H)_3$—10-H-7,8-R,R´—*nido*-7,8-$C_2B_9H_6$ (R, R´ = H, $PhCH_2$) were synthesized by the direct method using the reaction of $Cl_2Ru(PPh_3)(Ph_2P(CH_2)_4PPh_2)$ with [7,8-R,R´-*nido*-7,8-$C_2B_9H_{10}$][K] in benzene. Unsubstituted *exo-nido*-ruthenacarborane (R, R´ = H) was used *in situ* for the synthesis of the dinuclear Ru-Cu *exo-closo* cluster of the formula *exo-closo*-$(Ph_3P)Cu(\mu\text{-}H)Ru(Ph_2P(CH_2)_4PPh_2)(\eta^5\text{-}C_2B_9H_{11})$. The isomerism of the complex and the crystal structure were studied by NMR spectroscopy and X-ray diffraction. The catalytic activity of the cluster in the atom transfer radical polymerization of methyl methacrylate was investigated.

Key words: dinuclear ruthenium copper carborane complexes, methyl methacrylate, controlled radical polymerization, crystal structure.

Relatively recently, it has been proposed that organometallic compounds belonging to homo- and heterobimetallic ruthenium complexes can be used as catalysts for the atom transfer radical polymerization (ATRP) of vinyl monomers.[1] In particular, it has been found that dinuclear ruthenium complexes based on $[RuCl_2(p\text{-cymene})]_2$ exhibit high activity in the controlled synthesis of narrow-polydispersity polymers based on (meth)acrylates and styrene.[2—4] From this point of view, bimetallacarboranes containing one or both ruthenium atoms would be promised. This is supported by the results of the research of mononuclear Ru^{II} and Ru^{III} *closo*-ruthenacarboranes with chelating diphosphine ligands,[5—9] which showed their efficiency as ATRP catalysts. In the present study, we synthesized the first chelate ruthenium-copper *exo-closo*-bimetallacarborane with the diphosphine ligand of the formula $[(Ph_3P)Cu(\mu\text{-}H)Ru(Ph_2P(CH_2)_4PPh_2)(\eta^5\text{-}C_2B_9H_{11})]$, investigated its structure and isomerism by X-ray diffraction and NMR spectroscopy, and tested the complex as a catalyst in the controlled synthesis of poly(methyl methacrylate).

Results and Discussion

It was found that the reaction of the known complex $Cl_2Ru(PPh_3)(Ph_2P(CH_2)_4PPh_2)$ (**1**)[10] containing the chelating diphosphine dppb ligand with *nido*-dicarbaundecaborate salts [7,8-R_2-*nido*-7,8-$C_2B_9H_{10}$][K] (**2**, R = H; **3**, R = $PhCH_2$) in benzene affords mononuclear *exo-nido* complexes **4** and **5**, respectively, of the general formula *exo*-5,6,10-$[RuCl(Ph_2P(CH_2)_4PPh_2)]$-5,6,10-$(\mu\text{-}H)_3$—10-H—7,8-$R_2$—*nido*-7,8-$C_2B_9H_6$ (Scheme 1). In the course of the isolation and purification by column chromatography on silica gel, unsubstituted complex **4** exhibited properties absolutely identical to those of the *exo-nido* complex, which has been synthesized previously by the replacement of the PPh_3 ligands in the *exo-nido* complex *exo*-5,6,10-$[RuCl(PPh_3)_2]$—5,6,10-$(\mu\text{-}H)_3$—10-H—*nido*-7,8-$C_2B_9H_8$ (**6**)[6,11] with the dppb ligand.[12] Thus, according to the ^1H and $^{31}P\{^1H\}$ NMR spectroscopic data, complex **4** exists as a mixture of geometric isomers (which is characteristic of all known three-bridge *exo-nido*-metallacarboranes[11—13]), and it is readily rearranged into the *closo* isomer 3,3-(dppb)—3-H—3-Cl—*closo*-3,1,2-$RuC_2B_9H_{11}$ (**7**)[12] in 80% yield during storage in benzene (see Scheme 1). Unlike **4**, its *C,C´*-dibenzyl-substituted

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* Dedicated to Academician of the Russian Academy of Sciences I. L. Eremenko on the occasion of his 60th birthday.

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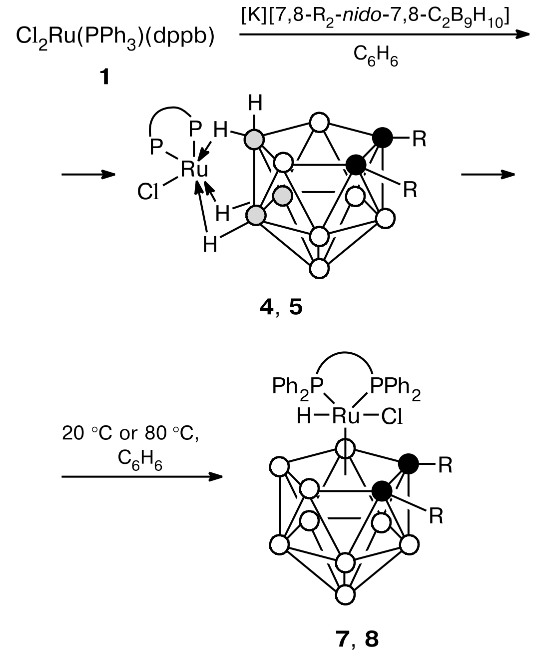
analog **5** was isolated from the reaction as air-stable orange crystals. Ruthenacarborane **5** does not undergo isomerization into the corresponding *closo* complex 3,3-(dppb)—3-H—3-Cl—1,2-$(PhCH_2)_2$-*closo*-3,1,2-$RuC_2B_9H_9$ (**8**) even upon heating in benzene. Complex **5** was characterized by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy and elemental analysis (see the Experimental section).

Scheme 1



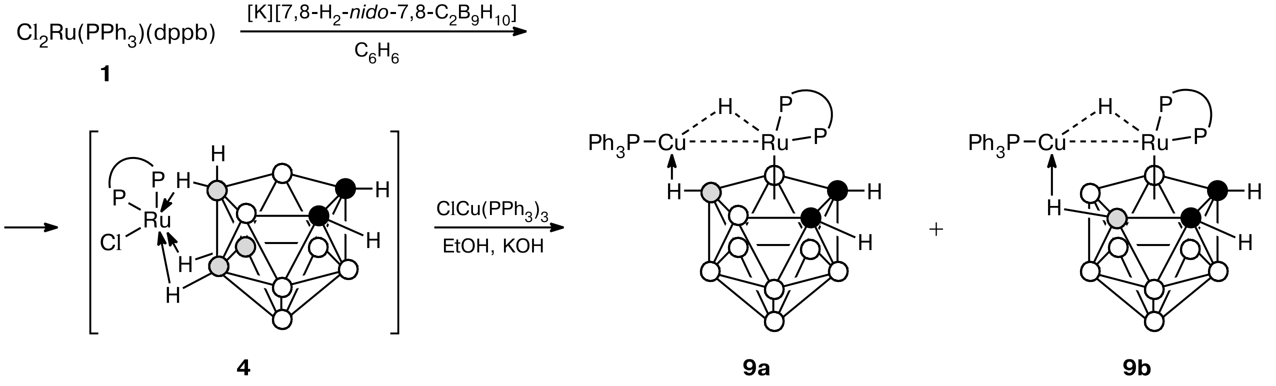
R = H (**4**, **7**), CH_2Ph (**5**, **8***); $\overset{\frown}{P\ P}$ = dppb = $Ph_2P(CH_2)_4PPh_2$

* Attempts to synthesize complex **8** failed.

Since unsubstituted complex **4** readily undergoes the *exo-nido→closo* rearrangement in solution, which hinders the isolation of **4** in the individual state, we used this complex *in situ* in the synthesis of the dinuclear Ru—Cu-*exo-closo* cluster with the chelating dppb ligand. The reaction was performed in one step according to Scheme 2 followed by the purification of the mixture of the isomeric products *exo-closo*-$(Ph_3P)Cu(\mu\text{-}H)Ru(Ph_2P(CH_2)_4PPh_2)(\eta^5\text{-}C_2B_9H_{11})$ (**9a**,**b**; the β- and α-site isomers, respectively) by the low-temperature (−5 °C) recrystallization from a THF—ethanol mixture. The composition and the structures of isomers **9a**,**b** in solution and in the solid state were determined by broad-band and selective ^{31}P-decoupled ^1H, $^{31}P\{^1H\}$, $^{11}B/^{11}B\{^1H\}$, and $^1H\{^{31}P\}$ NMR spectroscopy and based on the X-ray diffraction data for the major β-site isomer **9a** (Fig. 1), whose single crystals were obtained by slow recrystallization of a mixture **9a**,**b** from a C_6H_6—*n*-hexane system at 20 °C.

The structure and the geometry of complex **9a** are presented in Fig. 1. Selected interatomic distances and bond angles are given in Table 1. Complex **9a** contains the icosahedral moiety {*closo*-3,1,2-C_2B_9Ru(dppb)}, to which the copper atom is coordinated by two bridging B—H...Cu and Ru—H—Cu bonds. The copper atom is additionally coordinated by one PPh_3 ligand. The three-center two-electron (2e,3c)-bond B(8)—H...Cu (Cu...B(8), 2.198(4) Å; Cu...H(8), 1.75(4) Å) is formed with the involvement of the boron atom B(8) from the upper pentagonal plane of the carborane ligand bound at the most electron-rich β position with respect to the cage carbon atoms C(1) and C(2). The possible involvement of the α-B(4) atom in the similar interaction with the copper-containing $Cu(PPh_3)$ moiety through the formation of the 2e,3c-bond B(4)—H...Cu is not confirmed by the observed Cu...B(4) (2.591(5) Å) and Cu...H(4) (2.65(4) Å) distances in the structure. In complex **9a**, the bond between the ruthenium and copper atoms, which is additionally spanned by the bridging hydrido ligand, can exist (Ru—Cu, 2.5846(5) Å; Ru—H_{bridge}, 1.58(4) Å; Cu—H_{bridge}, 1.96(4) Å). However, it is difficult to conclusively prove the presence or absence of the metal—metal bond in complex **9a** without chemical quantum calculations of this bond order.**[14]** On the whole, the investigation of the structure of complex **9a** showed that the latter can be assigned to *exo-closo* clusters

Scheme 2



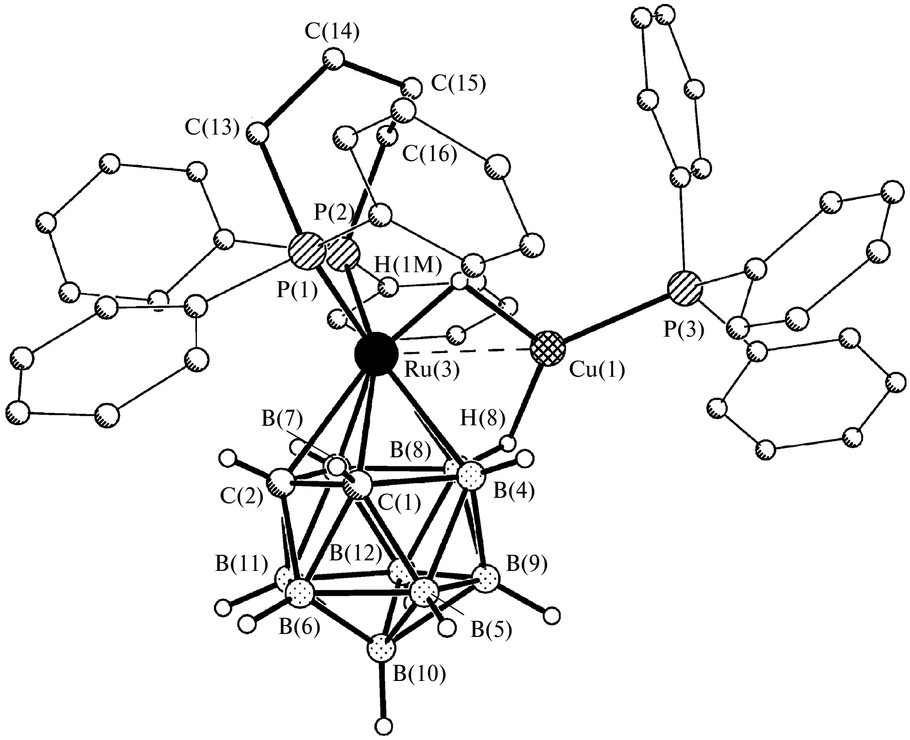


Fig. 1. Molecular structure of complex **9a**.

and confirmed that the formation of **9a** from *exo-nido*-ruthenacarborane **4** is accompanied by the mild *exo-nido→closo* rearrangement.

The structures of complexes **9a**,**b** in solution were studied by NMR spectroscopy of a mixture of the isomers (5 : 1) in C_6D_6. In the $^{31}P\{^1H\}$ NMR spectrum of **9a**,**b**, the singlets of the phosphine ligands at the ruthenium and copper atoms substantially differ in the linewidth and position. Thus, the major isomer **9a** is characterized by singlets at δ +48.50 (s, 2 P, dppb—Ru), +4.05 (s.br, 1 P, PPh_3—Cu), whereas the minor isomer **9b** gives singlets at δ +53.9 (s, 2 P, dppb—Ru), +3.3 (s.br, 1 P, PPh_3—Cu). In the high-field region of the ^1H NMR spectrum, each isomer shows one doublet of triplets of the bridging hydride Cu—H—Ru at δ –9.38 (major isomer **9a**) and –8.45 (minor isomer **9b**) (Fig. 2, *a*), which is transformed into singlets in the broad-band ^{31}P-decoupled $^1H\{^{31}P\}$ NMR spectrum (see Fig. 2, *b*). The selective ^{31}P-decoupled NMR spectra show doublets with the spin-spin coupling constants $^2J(H,P_{PPh_3})$ = 10.0 Hz (major isomer **9a**) and $^2J(H,P_{PPh_3})$ = 8.5 Hz (minor isomer **9b**) (see Fig. 2, *c*, *d*) of the dppb ligands for both isomers, whereas the ^{31}P decoupling at δ 3.3—4.05 leads to triplets with the spin-spin coupling constants $^2J(H,P_{dppb})$ = 24.9 Hz (major isomer **9a**) and $^2J(H,P_{dppb})$ = 25.4 Hz (minor isomer **9b**) for the PPh_3 ligands (see Fig. 2, *e*). Although the presence of the B—H...Cu bond in the crystal structure of complex **9a** was unambiguously established (see the X-ray diffraction data), the hydride signal of this bond at δ –20—0 is not observed in the ^1H NMR spectrum. This signal would be expected to be relatively broad due to the spin-spin coupling of ^1H with the magnetic nuclei ^{11}B, ^{10}B, and ^{63}Cu and, consequently, would coalesce with the baseline.[15] The expected set of closely spaced signals for the protons of the dppb and PPh_3 ligands, the Ph groups of diphosphines, and the cluster CH groups of both isomers **9a**,**b** is observed in the aliphatic and aromatic regions of the ^1H NMR spectrum;

Table 1. Selected bond lengths (*d*) and bond angles (ω) in the structure of **9a**

Parameter	Value	Parameter	Value
Bond	*d*/Å	Bond	*d*/Å
Ru(3)—C(1)	2.236(4)	Cu(1)...H(4)	2.65(4)
Ru(3)—C(2)	2.252(4)	C(1)—C(2)	1.607(7)
Ru(3)—B(4)	2.273(5)	C(1)—B(4)	1.668(7)
Ru(3)—B(7)	2.236(5)	C(2)—B(7)	1.698(7)
Ru(3)—B(8)	2.286(4)	B(7)—B(8)	1.793(7)
Ru(3)—P(1)	2.3006(12)	B(4)—B(8)	1.798(7)
Ru(3)—P(2)	2.2891(12)	Angle	ω/deg
Ru(3)—Cu(1)	2.5846(5)		
Ru(3)—H(1M)	1.58(4)	P(2)—Ru(3)—P(1)	91.61(4)
Cu(1)—H(1M)	1.96(4)	Ru(3)—H(1M)—Cu(1)	93(1)
Cu(1)—P(3)	2.1930(11)	Cu(1)—H(8)—B(8)	101(2)
Cu(1)...B(8)	2.198(4)	P(3)—Cu(1)—H(8)	124(2)
Cu(1)...B(4)	2.591(5)	P(3)—Cu(1)—H(1M)	118(2)
Cu(1)—H(8)	1.75(4)	H(1M)—Cu(1)—H(8)	117(2)

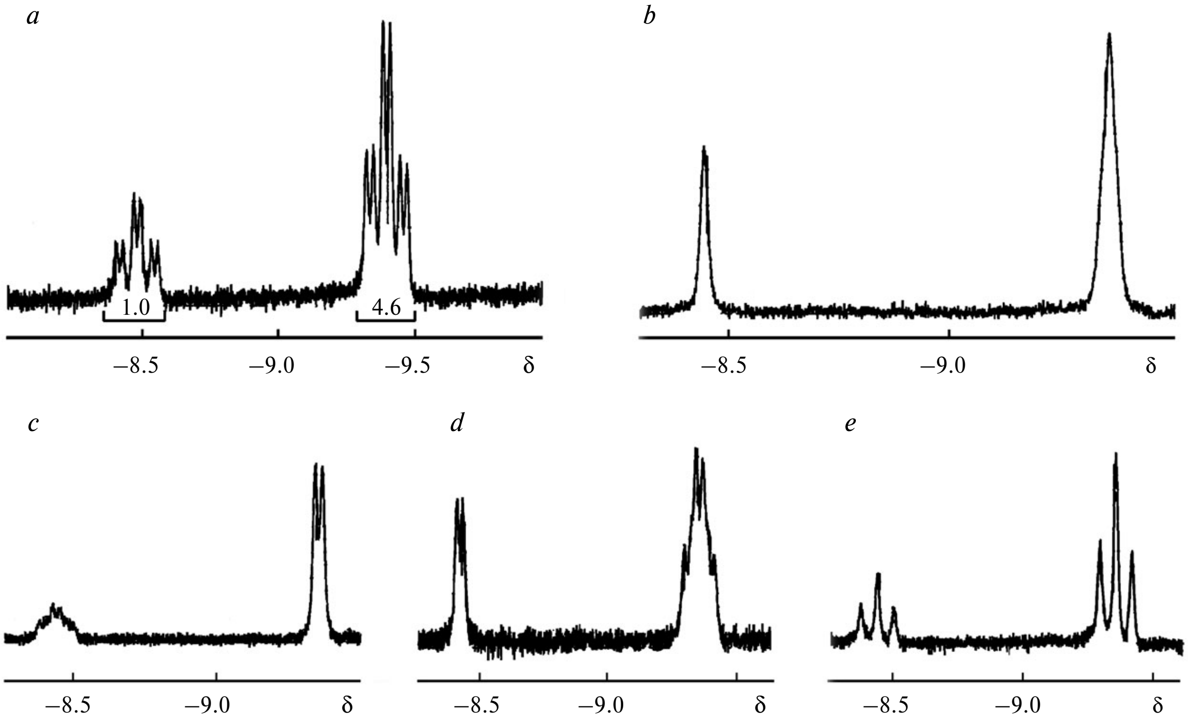


Fig. 2. The ^1H and $^1H\{^{31}P\}$ NMR spectra (hydride region) of a mixture of complexes **9a**,**b**: the ^1H NMR spectrum (the integrated intensities of the signals of isomers **9a**,**b** are given) (*a*); the broad-band decoupled $^1H\{^{31}P\}$ NMR spectrum (*b*); the ^{31}P-decoupled NMR spectrum of the dppb ligand of the major isomer **9a** (*c*); the ^{31}P-decoupled NMR spectrum of the dppb ligand of the minor isomer **9b** (*d*); the ^{31}P-decoupled NMR spectrum of the PPh_3 ligand of both isomers **9a**,**b** (*e*).

the signals of the cluster CH groups can be identified based on the linewidths (see the Experimental section).

The cluster obtained as a mixture of isomers **9a**,**b** was examined as the catalyst for controlled ATRP of methyl methacrylate (MMA). Carbon tetrachloride was used as the initiator for the radical generation. Our experiments showed that the catalytic system based on **9a**,**b** and CCl_4 can initiate the polymerization of MMA. At 80 °C, the reaction proceeds smoothly to high degrees of conversion without the gel effect (Fig. 3). The resulting polymers are characterized by low molecular weights but by a rather narrow molecular weight distribution (Fig. 4). The molecular weight of the polymers linearly increases with the conversion, and the molecular weight distribution of the samples becomes slightly narrower, which is characteristic of the controlled radical polymerization.[1,4]

At the same time, the linear plot of the molecular weight of polyMMA *versus* the conversion starts from the non-zero value (see Fig. 4), which indirectly indicates that the initial step of the reaction is accompanied by side processes, which are apparently associated with the *in situ* formation of the catalyst responsible for the chain growth. The side processes are also evidenced by the time dependence of the logarithm of the initial to current concentration ratio, which is nonlinear and is characterized by an inflection point in the initial region (see Fig. 3). An analysis of the plot $\ln(M_0/M)$ *versus* the time shows that the maximum number of active chains is observed in the initial polymerization step and it decreases with time.

A relatively large number of chains in the initial polymerization step is apparently associated with the irreversible reaction of complex **9** with CCl_4 giving radicals, which initiate the process, and producing ruthenium and copper complexes, which mediate the controlled ATRP polymerization.[7]

Taking into account the observed features of the radical polymerization of MMA in the presence of dinuclear chelate complex **9**, it was of interest to study the synthesis of polyMMA in the presence of the structurally similar non-chelate bimetallacarborane, *exo-closo*-$(Ph_3P)Cu(\mu\text{-}H)Ru(PPh_3)_2(\eta^5\text{-}C_2B_9H_{11})$ (**10**),[15] containing triphenylphosphine ligands at the Cu and Ru atoms. The results of the research (Table 2) show that the polymerization in

Table 2. Polymerization of MMA in the presence of **10** (0.125 mol.%) and CCl_4 (0.25 mol.%) at 80 °C

t/h	Conversion	M_n	M_w	M_w/M_n
0.5	30.2	9900	22200	2.2
5	54.6	25000	43100	1.7
50	99.0	40700	77900	1.9

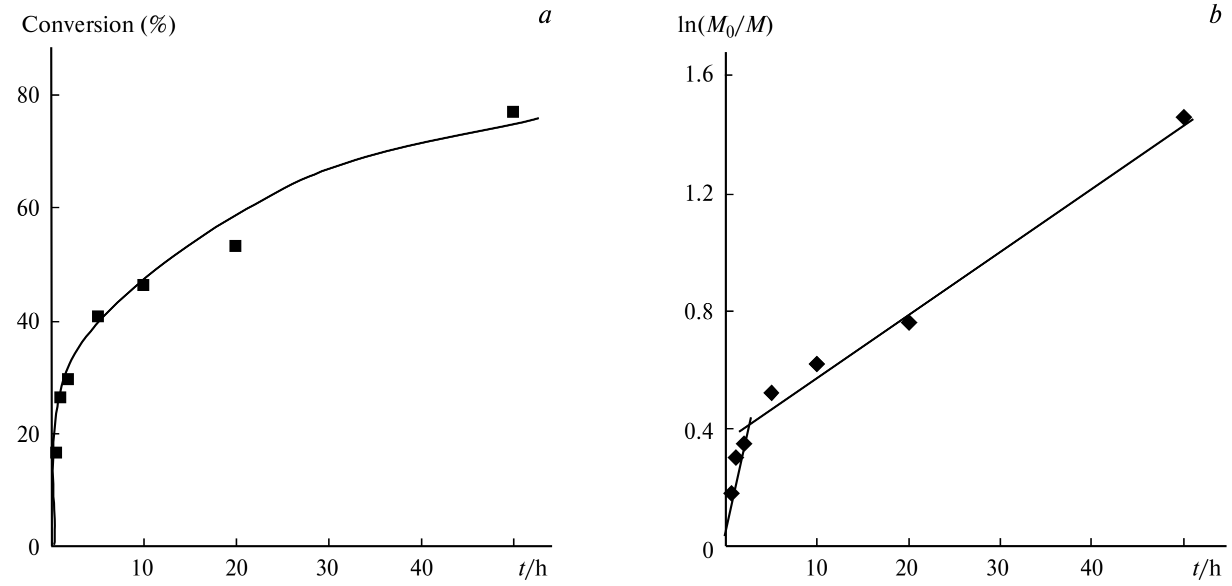


Fig. 3. Polymerization of MMA in the presence of the system based on **9** (0.125 mol.%) and CCl_4 (0.25 mol.%) at 80 °C: *a*, the plot of the conversion *versus* the time, *b*, the plot of ln(M_0/M) *versus* the time.

the presence of the dinuclear complexes with dppb and PPh_3 ligands is characterized by similar features. The molecular weight of the polymers increases, whereas the polydispersity decreases with increasing conversion. The polydispersity indices of the samples prepared in the presence of chelate complexes **9a**,**b** are somewhat smaller than those of the samples obtained in the presence of non-chelate bimetallacarborane **10**. Previously,[7—9] when studying the polymerization of vinyl monomers in the presence of mononuclear ruthenium carborane complexes with mono- and diphosphine ligands, we have observed a similar situation, *i.e.*, ruthenacarboranes with chelating diphosphines provide the more efficient control over the molecular weight distribution of polyMMA and polystyrene.[5—7] However, complexes **9** and **10** proved to be thermally less stable in the ATRP process, which is indirectly evidenced by the fact that the time dependence of the logarithm of the initial to current concentration ratio of the monomer deviates from the linear dependence.

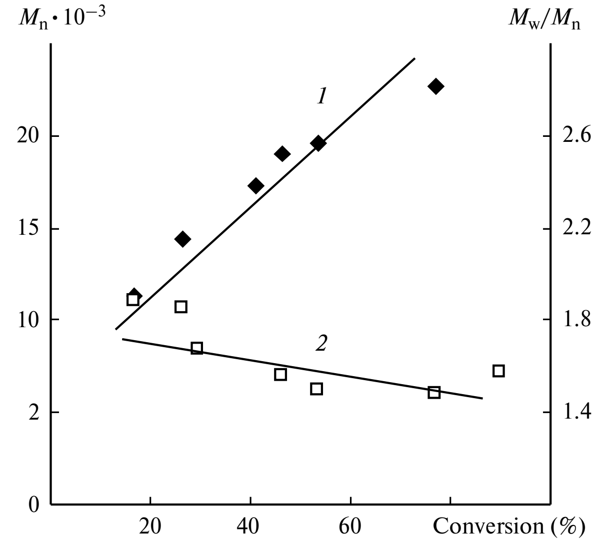


Fig. 4. Plots of the average molecular weight (M_n, *1*) and the polydispersity index (M_w/M_n, *2*) *versus* the conversion of polyMMA samples synthesized in the presence of the system based on **9** (0.125 mol.%) and CCl_4 (0.25 mol.%) at 80 °C.

To sum up, based on the experimental data it can be concluded that, although the systems under study are less efficient and stable in the ATRP of MMA than mononuclear *closo*-ruthenacarboranes,[5—8] a considerable advantage of these systems is that they provide a higher rate of the polymerization of MMA compared to mono-*closo*-ruthenacarboranes due apparently to the higher reactivity of the dinuclear systems with respect to CCl_4. Hence, it can be suggested that the dinuclear clusters with carborane ligands under consideration are promising catalysts for the polymerization of vinyl monomers when they are used at low concentrations. This is an important problem of the controlled synthesis of macromolecules under radical initiation conditions[1,4] and will be the subject of our further research.

Experimental

All reactions were carried out under an argon atmosphere with the use of anhydrous solvents prepared according to standard procedures. The products were isolated and purified by column chromatography on silica gel (Merck, 230—400 mesh). The NMR spectra were recorded on a Bruker AMX-400 NMR spectrometer (^{1}H, 400.13 MHz; ^{31}P, 161.98 MHz; ^{11}B, 128.3

MHz). The elemental analysis of new compounds was carried out in the Laboratory of Microanalysis of the A. N. Nesmeyanov Institute of Organoelement Compounds of the Russian Academy of Sciences. The bulk polymerization of MMA was performed under a residual pressure of 1.3 Pa according to a procedure described previously.[9] The molecular weight characteristics of the polymers were determined by gel permeation chromatography on a Knauer instrument (Germany) equipped with a Phenomenex Linear-2 linear column (USA) and an RI Detector K-2301 differential refractometer as the detector. Chloroform was used as the eluent. The calibration was carried out with the use of narrow-polydispersity polyMMA standards (Waters; the molecular weight varies from 2580 to $9.81 \cdot 10^5$). The chromatographic data were interpreted using the ChromGate software.

***exo*-Chloro[1´,4´-bis(diphenylphosphino)butane]-*nido*-[7,8-dibenzyl-10-hydro-*ortho*-carborane-5,6,10-tris(hydrido)]ruthenium (5, a mixture of symmetric (*s*) and asymmetric (*as*) isomers in a ratio of 1.3 : 1).** A mixture of complex **1** (0.2 g, 0.233 mmol) and K salt **3** (0.09 g, 0.256 mmol) in benzene (15 mL) was stirred at room temperature for 2 h until the color of the solution changed from dark-green to orange. The reaction mixture was concentrated *in vacuo* to 2—3 mL and then transferred to a column packed with silica gel using benzene as the eluent. The subsequent evaporation of the solvent *in vacuo* and the recrystallization of the residue from a benzene—*n*-hexane mixture afforded analytically pure crystals of a mixture of *s* and *as* isomers **5** in a yield of 0.16 g (79%). Found (%): C, 62.96; H, 6.11; B, 11.00. $C_{44}H_{52}B_9ClP_2Ru \cdot C_6H_6$. Calculated (%): C, 62.91; H, 6.08; B, 10.19. ^1H NMR (CD_2Cl_2, 20 °C), δ: –17.2 (m, H(10), *s*-**5**); –15.7 (m, H(6) or H(5), *as*-**5**); –5.8 (m, H(10), *as*-**5**); –4.0 and –3.3 (both m, H(5) or H(6), *as*-**5** and H(5), H(6), *s*-**5**); –1.2 (m, H_{extra}, *s*-**5** and *as*-**5**); 1.61, 2.05, 2.42, and 3.41 (all br.s, $(PCH_2C\underline{H}_2)_2$, *s*-**5**); 1.48, 1.85, 2.37, 2.50, 3.25, and 3.66 (all br.s, $(PCH_2CH_2)_2$, *as*-**5**); 3.09—3.21 (two overlapping q (7 lines), 2 $PhC\underline{H}_2$); 7.12—7.61 (m, Ph). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C), δ: 52.02 (m, *as*-**5**); 53.05 (br.s, *s*-**5**); 57.29 (br.d, *as*-**5**, $J_{P,P}$ = = 39.3 Hz). ^{11}B NMR (CD_2Cl_2, 20 °C), δ, $J = J_{B,H}$/Hz: +4.4, +1.2, –7.8, –20.7, and –32.4 (all br.s, B(1)—B(4) *s*- and *as*-**5**; B(5) *as*-**5**); –18.8, –24.5, –26.6 (d of different intensities, B(5), B(6), *s*-**5**, B(9), B(11) *s*-**5**, *as*-**5**, *J* = 76, 99, 110 Hz); 41.2, (m, B(10), *s*-**5**); 44.6 (t, B(6), *as*-**5**, *J* = 86 Hz).

***exo*-Chloro[1´,4´-bis(diphenylphosphino)butane]-*nido*-[10-hydro-*ortho*-carborane-5,6,10-tris(hydrido)]ruthenium (4, a mixture of symmetric (*s*) and asymmetric (*as*) isomers).** Ruthenacarborane **4** was formed as a mixture of *s* and *as* isomers under conditions similar to those described above for complex **5** starting from complex **1** (0.150 g, 0.174 mmol) and K salt **2** (0.033 g, 0.19 mmol) in benzene. Upon storage in solution, *exo-nido* complex **4** was transformed into the known *closo* isomer (**7**).[12] An attempt to isolate complex **4** in the individual state failed because of its irreversible transformation in solution into *closo* isomer **7**, although the *exo-nido* and *closo* isomers emerged from a column packed with silica gel as individual bands: the lower orange band (a mixture of the *s* and *as* isomers of **4**) and the upper yellow band (the *closo* isomer). The reaction was monitored by $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C), δ: 37.3 (s, **7**); 53.6 (s, *s*-**4**); 52.4 and 57.4 (both br.m, *as*-**4**) or by the analysis of the high-field signals in the ^1H NMR spectrum (C_6D_6, 20 °C), δ: –16.6 (m, H(10), *s*-**4**); –15.0 (m, H(6), *as*-**4**); –7.9 (td, RuH, **7**); –5.4 (m, H(10), *as*-**4**); –3.3 (m, H(5), H(6), *s*-**4**); –2.5 (m, H(6), *as*-**4**); –1.2 (m, H_{extra}, *s*-**4**, *as*-**4**).[12] In subsequent experiments, complex **4** was used *in situ* as the reactant.

Synthesis of the dinuclear cluster *exo-closo*-$(Ph_3P)Cu(\mu\text{-}H)\text{-}Ru(Ph_2P(CH_2)_4PPh_2)(\eta^5\text{-}C_2B_9H_{11})$ (9a,b, a mixture of isomers, 5 : 1). A mixture of complex **1** (0.2 g, 0.233 mmol) and K salt **2** (0.07 g, 0.407 mmol) in dry C_6H_6 (20 mL) was stirred at room temperature for 1 h. The solvent was removed *in vacuo*, and an excess of powdered KOH (0.07 g, 1.25 mmol) was added to the residue. The pumping of the mixture of the reactants was carried out until all traces of air were removed. The reactor was filled with argon, anhydrous ethanol (15 mL) was added, and the reaction mixture was stirred for 30 min until a yellow precipitate formed. Then $ClCu(PPh_3)_3$ (see Ref. 16) (0.18 g, 0.20 mmol) and anhydrous THF (5 mL) were added to the reaction mixture, and the mixture was stirred for 2.5 h. A dirty-yellow precipitate that formed was filtered off and washed with anhydrous diethyl ether (2×3 mL). The product was purified by recrystallization from a C_6H_6—*n*-hexane mixture. Dinuclear Ru—Cu-complex **9a**,**b** (a 5 : 1 mixture of isomers) was obtained as yellow needle-like crystals in a yield of 0.18 g (75%). Found (%): C, 60.45; H, 5.29. $C_{48}H_{55}B_9CuP_3Ru \cdot C_6H_6$. Calculated (%): C, 60.89; H, 5.73. IR, ν/cm^{-1}: 2542 (B—H). ^1H NMR (C_6D_6, 20 °C), δ: –9.39 (td, 1 H, Ru—H—Cu, **9a**, $^2J(H,P_{PPh_3})$ = 10.0 Hz, $^2J(H,P_{dppb})$ = 24.9 Hz); –8.47 (td, 0.2 H, Ru—H—Cu, **9b**, $^2J(H,P_{PPh_3})$ = 8.5 Hz, $^2J(H,P_{dppb})$ = 25.4 Hz); 1.44, 2.32, 2.47, 2.55 (m of different intensities with Σ = 9.8 H, $(PC\underline{H}_2C\underline{H}_2)_2$, **9a**,**b**); 1.86 (br.s, >2 H, CH_{carb}, **9a**,**b**); 6.75—7.85 (set of eleven t and one br.m, 42 H, **9a**,**b**). $^1H\{^{31}P\}$ NMR (C_6D_6, 20 °C), δ: –9.39 (s, Ru—H—Cu, **9a**); –8.47(s, Ru—H—Cu, **9b**); 1.44, 2.32*, 2.47*, 2.55 (m of different intensities, Σ = 9.8 H, $(PC\underline{H}_2C\underline{H}_2)_2$, **9a**,**b**); 1.86 (br.s, 2 H, CH_{carb}, **9a**); 6.79 (t, 3 H, *J* = 7.4 Hz); 6.86 (t, 3 H, *J* = 7.4 Hz); 6.93 (t, 2 H, *J* = 7.2 Hz); 7.02—7.22 (m, 18 H); 7.43 (m, 3 H); 7.53 (d, 3 H, *J* = 7.6 Hz); 7.62 (d, 3 H, *J* = 7.3 Hz); 7.75—7.83 (m, 6 H); 7.85 (d, 1 H, *J* = 7.4 Hz). $^{31}P\{^1H\}$ NMR (C_6D_6, 20 °C), δ: 3.33 (br.s, $\underline{P}Ph_3$, **9b**); 4.05 (br.s, $\underline{P}Ph_3$, **9a**); 48.53 (s, $(PCH_2CH_2)_2$, **9a**); 53.9 (s, $(PCH_2CH_2)_2$, **9b**).

X-ray diffraction study of complex 9a. Crystals ($C_{57}H_{64}B_9CuP_3Ru$, *M* = 1103.89) are orthorhombic, space group $P2_12_12$, at 100 K *a* = 14.0546(5) Å, *b* = 34.6252(13) Å, *c* = 10.9995(4) Å, *V* = 5352.8(3) Å^3, *Z* = 4, d_{calc} = 1.370 g cm^{-3}, μ(Mo-*K*α) = 8.07 cm^{-1}. The intensities of 52200 reflections (10484 independent reflections, R_{int} = 0.0852) were measured on a Bruker APEX II diffractometer equipped with an area detector[17] (graphite monochromator, λ(Mo-*K*α) = 0.71073 Å, ω-scanning mode, $2\theta_{max}$ = 52°, *T* = 100 K). The structure was solved by direct methods and refined by the full-matrix least-squares method based on F^2_{hkl} with anisotropic displacement parameters for all nonhydrogen atoms. The absolute configuration was determined based on the Flack parameter (*x* = 0.00(2)).[18] The hydrogen atoms of the carborane moiety and the hydride ligand were located in difference Fourier maps. The other hydrogen atoms were positioned geometrically and refined using a riding model. In the crystal structure, there are two benzene solvent molecules, one of which is in a general position, and another molecule occupies a special position on a twofold axis. The bridging methylene fragment of the complex is disordered with occupancies of 60 and 40%. The final *R* factors are R_1 = 0.0414 (based on F_{hkl} for 8366 reflections with $I > 2\sigma(I)$), wR_2 = 0.0840, and *S* = 1.046 (based on F^2_{hkl} for all

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* Signals with a changed multiplicity.

independent reflections). All calculations were carried out on a PC with the use of the SHELXTL program package.[19] The complete tables of atomic coordinates, bond lengths, bond angles, and anisotropic thermal parameters were deposited with the Cambridge Structural Database.

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